



TITLE:

MOLECULAR WEIGHT DEPENDENCE OF EQUILIBRIUM  
MELTING TEMPERATURE AND CRYSTALLIZATION PROCESS  
OF LOW MOLECULAR WEIGHT POLY (ETHYLENE OXIDE)  
(PEO) IN PEO/POLY (METHYL METHACRYLATE) (PMMA)  
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Introduction

Melting point depression of crystalline/amorphous polymer blend is thought to be represented by the following equation derived by Nishi and Wang:

$$1/T_{mb}^0 - 1/T_{mh}^0 = -(RV_{2u})/(\Delta H_u V_{1u})[\ln \phi_2/m_2 + (1/m_2 - 1/m_1)\phi_1 + \chi \phi_1^2] \quad (1)$$

where  $T_{mb}^0$  and  $T_{mh}^0$  are the equilibrium melting temperature of blend and crystalline polymer, respectively,  $R$  the gas constant, subscripts 1 and 2 represent amorphous and crystalline components, respectively,  $V_{iu}$  the molar volume,  $\Delta H_u$  the heat of fusion of repeating unit per mol of crystalline polymer,  $\phi_i$  the composition ( $\phi_1 + \phi_2 = 1$ ),  $m_i$  the degree of polymerization and  $\chi$  the interaction parameter between component polymers.<sup>1)</sup> On the other hand, crystallization process is expected to be affected by amorphous component through changes of the surface free energy of the crystal, the mobility of polymer chain of the crystalline component and so on.

This study aims at investigating molecular weight dependence of equilibrium melting temperature and crystallization rate of poly(ethylene oxide) (PEO) in PEO/poly(methyl methacrylate) (PMMA) blends in low molecular weight region of PEO.

Experimental

Weight average molecular weights,  $Mw_{PEO}$ , of PEOs were  $Mw_{PEO} = 1.5 \times 10^3$ ,  $3.7 \times 10^3$ ,  $5.2 \times 10^3$  and  $1.1 \times 10^4$ , respectively.  $Mw_{PMMA}$  of PMMA used was  $Mw_{PMMA} = 2.2 \times 10^5$ . All these samples have narrow distributions of molecular weight. The composition of blends studied here was 20PMMAwt%. Isothermal crystallization process and melting point were measured by differential scanning calorimetry (DSC). Half time of crystallization  $t_{1/2}$ , which was the time for the crystallinity to become 50%, was evaluated as the measure of the crystallization rate, and melting point was determined by the peak temperature of the melting curve.

Results and Discussion

Two melting temperatures were observed for PEO. It is well known that plural kinds of crystals with different integral number of folding  $n$  ( $n = 0, 1, 2, \dots$ ) named integral folding crystal (IF crystal) are formed in low molecular weight fraction of PEO.<sup>2)</sup> The high and low melting temperatures seem to correspond with the melting temperatures of IF crystals with  $n = 0$  (IF( $n = 0$ )) and 1 (IF( $n = 1$ )), respectively, from the comparison of the data with the literature.<sup>2)</sup> On the other hand, only one melting temperature of IF( $n = 0$ )

was observed and no clear melting curve corresponding to IF( $n = 1$ ) was observed for blends. The extent of the melting point depression,  $1/T_{mb}^0 - 1/T_{mh}^0$ , for IF( $n = 0$ ) crystals became large with  $Mw_{PMMA}$  increased, and hence eq.(1) did not hold. Generally, equilibrium melting temperature of infinitely spreading crystal with finite thickness of lamella,  $L$ , is described by

$$T_m^0(L) = T_m^0(\infty)[1 - 2\sigma_e/\Delta H_m L] \quad (2)$$

where  $T_m^0(\infty)$  is the equilibrium melting temperature of the crystal with  $L = \infty$ ,  $\sigma_e$  the surface free energy of end (or fold) surface of crystal lamella and  $\Delta H_m$  the heat of fusion per unit volume of the crystal.<sup>3)</sup> Fig.1 shows  $1/L$ -dependence of  $T_{mh}^0$  and  $T_{mb}^0$ .  $L$  was calculated by using the relation  $L = Mw/158$  (nm).<sup>2)</sup> Equilibrium melting temperatures for both of PEO and blend change linearly with  $L^{-1}$  according to eq.(2). The slope of the figure for PEO is slightly larger than that for blend. The difference of the slopes makes the difference between  $T_{mh}^0$  and  $T_{mb}^0$  smaller with  $Mw_{PEO}$  decreases. According to eq.(2), the values of the slopes in Fig.1 correspond to the values of  $2T_m^0(\infty)\sigma_e/\Delta H_m$  for PEO and blend, respectively. The slopes in Fig.1 are 181 and 164 for PEO and blend, respectively.

Activation energy  $E_a$  for formation of secondary nucleus in crystallization process was evaluated according to  $t_{1/2} = \tau \exp(E_a/\Delta T_m)$ .<sup>4)</sup>  $\Delta T_m$  is the temperature variable representing the temperature difference between  $T_m^0$  and the

crystallization temperature  $T_c$ , i.e.,  $\Delta T_m \equiv |T_m^0 - T_c|$ .  $E_a$  is related to  $\sigma_e$ , the surface free energy  $\sigma_s$  of side surface of crystal lamella and  $\Delta H_m$  by the relation:<sup>3)</sup>

$$E_a \propto \sigma_e \sigma_s / \Delta H_m.$$

Therefore, the value of  $E_a$  is expected to be changed by blending PMMA. However, experimentally evaluated  $E_a$  was not largely changed by blending PMMA. Since the change of the slope in Fig.1 by blending PMMA is not so large, the change of  $E_a$  by blending PMMA may not be detected.

#### References

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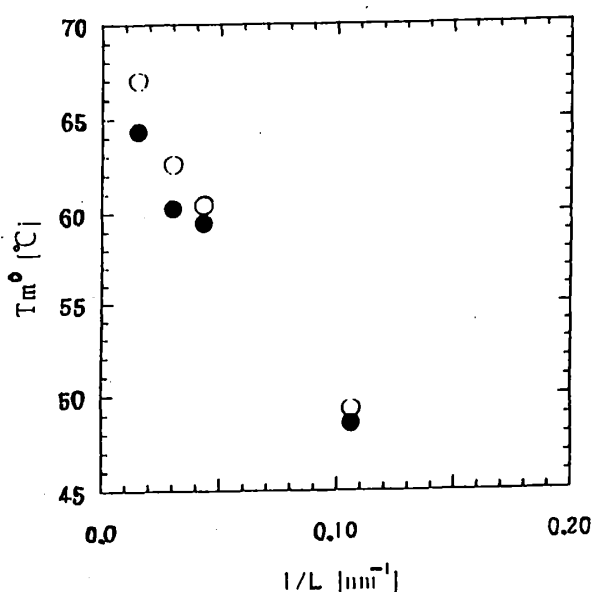


Fig.1 Plots of  $T_{mh}^0$  (○) and  $T_{mb}^0$  (●) versus inverse of lamella thickness  $L$ .